

Health & Safety Manual

Supplement 21.01

Chemical Hygiene Plan For Laboratories

February 1994

Approved by the ES&H Working Group

_____ date _____
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Chemical Hygiene Plan for Laboratories*

Contents

1.0	Introduction	1
1.1	Background	1
1.2	Applicability	2
1.3	Chemical Hygiene Plan Regulatory Synopsis	2
2.0	Responsibilities for Chemical Hygiene	4
2.1	Associate Director	4
2.2	Assurance Manager	4
2.3	Chemical Hygiene Officer	4
2.4	Facility Manager	5
2.5	Responsible Individual.....	5
2.6	Laboratory/Room Responsible Person.....	5
2.7	Employee	6
2.8	ES&H Team	6
3.0	Safety Procedures and Standard Work Practices	6
3.1	Safety Procedures	6
3.2	Standard Work Practices	6
3.2.1	General Rules	7
3.2.2	Selection of Chemicals	8
3.2.3	Hazard Identification.....	8
3.2.4	Personal Protective Equipment	9
3.2.5	Emissions to the Environment	9
3.2.6	Spills and Accidents.....	9
3.2.7	Storage	10
3.2.8	Waste Disposal	11
4.0	Criteria for Determining and Implementing Control Measures to Reduce Employee Exposure to Hazardous Chemicals.....	11
4.1	Types of Controls	11
4.2	Selection of Controls	12
5.0	Ensuring Performance of Fume Hoods and Other Protective Equipment	12
6.0	Employee Information and Training.....	13
6.1	Required Information	13
6.1	Required Training	14
7.0	Preapproval of Operations.....	14
8.0	Medical Consultation and Examination	15
9.0	Designation of Chemical Hygiene Officer.....	16
10.0	Additional Protection for Particularly Hazardous Substances	16
10.1	General.....	16
10.2	Additional Protection Required	17

Appendix A	Terms and Definitions.....	19
Appendix B	Sample Form for Providing Information to Employees.....	25
Appendix C	Safety Practices and Procedures for Working with Chemicals.....	26

LLNL Chemical Hygiene Plan for Laboratories

1. Introduction

The LLNL Chemical Hygiene Plan for Laboratories is required by 29 CFR 1910.1450 (Occupational Exposure to Hazardous Chemicals in the Laboratory) under the Occupational Safety and Health Administration (OSHA). This regulation (referred to herein as the OSHA Laboratory standard) covers occupational exposure to hazardous chemicals in laboratories. As such, it complements, replaces, or supersedes other OSHA requirements regulating the control of hazardous substances.

This supplement contains

- The LLNL Chemical Hygiene Plan for facilities.
- Requirements for the plan based on OSHA regulations and/or LLNL policy.
- Responsibilities for complying with the OSHA laboratory standard.
- Appendix A, which contains the terms and definitions used in this supplement.
- Appendices B and C, which are nonmandatory guidance unless noted otherwise.

Where chemicals are used in laboratories, specific details for implementing this Chemical Hygiene Plan shall be included in the facility safety procedure (FSP). Very specific details about individual procedures may be covered in operational safety procedures (OSPs). By reference, the *Health & Safety Manual* and the Environmental Protection Handbook are part of the LLNL Chemical Hygiene Plan.

1.1 Background

Before 1990, OSHA's approach to controlling occupational exposures to hazardous chemicals was to develop lists of permissible exposure limits (PELs), substance-specific standards, and the health hazard communication standard (29 CFR 1910.1200; see Supplement 7.02 [formerly Supplement 1.02] of the *Health & Safety Manual*). These regulations address industrial applications where workers typically receive prolonged exposure to large quantities of a few chemicals.

The OSHA laboratory standard (enacted in 1991) applies to all employees engaged in the use of hazardous chemicals in laboratory workplaces where short-term exposure to varying amounts of such chemicals may be encountered. This standard emphasizes worker training and safe work practices.

1.2 Applicability

The OSHA laboratory standard only applies to laboratory workplaces where chemicals are used in a nonroutine, nonproduction manner by workers with at least some education and training in science. Examples of where this standard applies at LLNL are chemistry, material science, and biology research laboratories. Workplaces not covered by this standard include photo labs that do not change chemical processes, electronics labs, machine shops, craft shops, and pilot plant operations that are or simulate a production operation in which chemicals will not change.

Laboratory use of hazardous chemicals is defined as the handling or use of hazardous chemicals in which all of the following criteria are met:

- Procedures using chemicals are carried out on a laboratory scale (e.g., using containers for reactions, transfers, and other handling of chemicals that are easily manipulated by one person).
- Multiple chemical procedures or chemicals are used.
- The operations involved are neither part of a production process nor simulate one.
- Protective laboratory practices and equipment are available and are commonly used to minimize the potential for employee exposure to hazardous chemicals.

When the operations in a particular facility meet all of the above criteria, that facility must comply with the requirements of this Chemical Hygiene Plan. Operations in facilities involved in the use of hazardous chemicals but do not meet the criteria previously outlined shall comply with the health hazard communication program described in Supplement 7.02, including all other applicable OSHA regulations.

1.3 Chemical Hygiene Plan Regulatory Synopsis

Below is a summary of the OSHA laboratory standard, which includes some modifications to comply with additional DOE orders.

1. Where hazardous chemicals (as defined by this standard) are used in the workplace, the employer shall develop and carry out the provisions of a written chemical hygiene plan that
 - Protects employees from the health hazards associated with hazardous chemicals in that laboratory.
 - Keeps exposures below the limits specified in DOE orders—the lower of the OSHA permissible exposure limits (PELs) or the threshold limit values (TLVs) identified by the American Conference of Governmental Industrial Hygienists (ACGIH).

2. The chemical hygiene plan shall be available to employees, employee representatives, and, upon request, regulatory agencies.

3. The chemical hygiene plan shall consist of the elements below, including measures that employers must take to ensure employee protection.

- Standard operating procedures that are relevant to health and safety. These procedures shall be followed when laboratory work involves the use of hazardous chemicals.
- The criteria employers will use to determine and implement control measures to reduce employee exposure to hazardous chemicals, including engineering controls, the use of personal protective equipment, and hygiene practices. Particular attention shall be given to the selection of control measures for chemicals that are known to be extremely hazardous (see also the last bulleted item in this section).
- A requirement that fume hoods and other protective equipment function properly, and that specific measures are taken to ensure proper and adequate performance of such equipment.
- Provisions for employees to receive information and the required training.
- The circumstances under which a laboratory operation, procedure, or activity will require prior approval from the employer (or his/her designee) before it can be implemented.
- Provisions for employees to receive consultation and medical examinations.
- Designation of the personnel responsible for implementing the chemical hygiene plan, including assignment of a chemical hygiene officer. Establishment of a chemical hygiene committee is recommended but not mandatory.
- Provisions for additional protection for employees who work with “particularly hazardous substances.” These include “select carcinogens,” reproductive toxins, and substances that have a high degree of acute toxicity.

The following provisions shall be given special considerations when appropriate:

- Establishment of a designated area.
- Use of containment devices, such as fume hoods or glove boxes.
- Development of procedures for safely removing contaminated waste and decontaminating equipment and facilities.

2.0 Responsibilities for Chemical Hygiene

2.1 Associate Director

The facility associate director (AD) has ultimate responsibility for environmental, safety, and health (ES&H) issues with the facility. Each AD having responsibility for chemical operations shall

- Determine which part of his/her operations is governed by the OSHA laboratory standard, and ensure that such operations comply with this Chemical Hygiene Plan.
- Develop an appropriate implementation plan, including procedures for complying with each element of training and information exchange and record keeping. The respective elements of the directorate's Chemical Hygiene Plan shall be included in applicable FSPs and, if necessary, in individual OSPs.

2.2 Assurance Manager

Each Ad appoints an assurance manager who reports to him/her. The assurance manager shall

- Oversee ES&H activities within the directorate.
- Be familiar with this Chemical Hygiene Plan.
- Review and monitor periodically implementation of the plan's elements at all applicable levels of the directorate organization.

2.3 Chemical Hygiene Officer

Appointed by the Hazards Control Department Head, the chemical hygiene officer for the Laboratory shall

- Provide technical guidance and assistance to all directorate organizations with the implementation of this Chemical Hygiene Plan.
- Prepare and maintain a list of particularly hazardous substances.
- Review and evaluate the effectiveness of the overall Chemical Hygiene Plan annually.
- Review and evaluate how effectively LLNL programs implement the plan.
- Recommend updates to the plan as necessary.

2.4 Facility Manager

All facility managers shall be familiar with this Chemical Hygiene Plan and its contents and objectives, and shall assure the appropriate implementation of the Plan's requirements.

2.5 Responsible Individual

LLNL refers to the person who has line responsibility for the environment, safety, and health in laboratories as the "responsible individual." Individuals who are so designated may not necessarily be responsible for *supervising* other personnel.

The responsible individual's primary chemical hygiene duties include

- Identifying the need for developing safety procedures and OSPs for each experiment.
- Being familiar with this Chemical Hygiene Plan and its applicability to his/her operations.
- Ensuring that all project personnel have been informed and trained on the work they are assigned, as required by the section entitled "Employee Information and Training" of this plan.
- Evaluating the project's potential for environmental emissions.

2.6 Laboratory/Room Responsible Person

The responsible individual for the laboratory workplace (usually a room) shall

- Review and understand planned experimental activities and the hazardous chemicals involved, including special personal protective equipment that may be required for those activities.
- Ensure that employees working within the laboratory know and follow the directorate's Chemical Hygiene Plan (e.g., the FSP) for their work area.
- Ensure that proper protective equipment is available and is in working order, and that the assigned staff has been trained in the proper use of such equipment.
- Know the operating limits of the FSP and when to prepare OSPs.
- Make periodic, informal chemical safety and housekeeping inspections and initiate corrective action where necessary.

2.7 Employee

Employees shall conduct each task (experiment) in accordance with the applicable FSP and OPS, including the institutional procedures identified in this Chemical Hygiene Plan.

2.8 ES&H Team

The area ES&H team shall provide technical support and guidance. This includes monitoring the workplace, evaluating hazards to select the appropriate respirators, providing formal and informal training, and recommending controls to minimize exposure and emissions to the environment.

3.0 Safety Procedures and Standard Work Practices

3.1 Safety Procedures

Safety procedures are prepared in accordance with the requirements of Chapter 2 of the *Health & Safety Manual*. FSPs cover the general hazards of a facility; OSPs are prepared for experiments that are not specifically authorized by the FSP or when required by the *Health & Safety Manual*. Employees who handle hazardous chemicals must follow established procedures for each laboratory.

Safety procedures shall be developed to satisfy parts of this Chemical Hygiene Plan, and their content must be consistent with this supplement. In particular, FSPs will be the primary documentation for how facilities shall implement this plan. Chapter 2 of the *Health & Safety Manual* describes when and how to prepare safety procedures. Additional guidance is available from your area ES&H team.

The *Health & Safety Manual* and the *Environmental Protection Handbook* provide required standard procedures for minimizing many of the hazards found in laboratory workplaces. Table 1 provides the operating procedures and guidance in these documents.

3.2 Standard Work Practices

All employees must follow standard work practices when handling hazardous materials. It is recommended that such practices be incorporated into written safety procedures when applicable. Additional recommendations are given in Appendix C to supplement these requirements.

<i>Health & Safety Manual</i>	Topic
Chapter 2	Work Planning, Safety Procedures, and Management Oversight
Chapter 5	Medical Program
Chapter 10	Personal Protective Program
Chapter 12	Ventilation
Chapter 21	Chemicals (also see the following sections in this chapter)
	Planning
	Material Safety Data Sheets
	Facilities and Equipment
	Storage of Chemicals
	Handling Solid and Liquid Chemicals
	Peroxidizable Materials
	Handling Gases
	Chemical Waste Disposal (see also Section 4 of the <i>Environmental Protection Handbook</i> .)
	Chemical Spills (see also Section 4 of the <i>Environmental Protection Handbook</i> .)
Supplement 21.10*	Safe Handling of Beryllium and Its Compounds
Supplement 21.11*	Safe Handling of Mercury
Supplement 21.12*	The Safe Handling of Fluorine
Supplement 21.13*	Hydrogen
Supplement 21.14*	Safe Handling of Alkali Metals
Supplement 21.15*	Safe Handling of Acids and Bases
Supplement 21.16A*	Safe Handling of Chemical Carcinogens in Research Laboratories
Chapter 25	Fire
Chapter 32	Pressure
<i>Environmental Protection Handbook</i>	Topic
Section 3A	Guidelines for discharge to the sanitary sewer system
Section 4C	Guidelines for waste accumulation areas
Section 4E	Preparation guide for generators of hazardous chemicals and radioactive waste at LLNL
Section 5	Guidelines for the permitting of air-pollution emission sources

* Provides additional details on the requirements for the safe handling of hazardous materials.

3.2.1 General Rules

- Never perform hazardous operations alone in a laboratory or chemical storage area.
- Wear appropriate eye protection at all times.

- Minimize exposure to all chemicals regardless of their familiarity. Because most laboratory chemicals have not been thoroughly tested for safety, their toxicity cannot be fully understood. Therefore, it is prudent to implement procedures that will reduce the likelihood of exposure. Skin contact should always be avoided.
- Assume that unknown materials are toxic, and that a mixture is more toxic than its most toxic component.
- Ensure that sources of ignition are not close or nearby when working with flammable materials. This will prevent a fire or explosion if a vapor release or liquid spill occurs.
- Use a tip-resistant shield for protection in case an explosion or implosion occurs.
- Do not apply cosmetics, eat, or drink in laboratories.
- Do not use mouth suction for pipetting or starting a suction.

3.2.2 Selection of chemicals

- Before a chemical compound is selected for use in an operation or process, the responsible individual identified in the FSP or OSP shall do the following:
 - Review the potential hazards of the substance to assess the conditions under which the compound will be used.
 - Determine if safer alternatives are available.
- The conditions in a laboratory at the time the process is being carried out must be considered before selecting a chemical. The following shall be evaluated:
 - Presence of incompatible chemicals.
 - Adequacy of the ventilation or containment system.
 - Presence of individuals during a high-risk operation.
 - Other conditions that may interfere with the precautions necessary for a substance or procedure.

3.2.3 Hazard Identification

- Labels on incoming containers shall not be removed or defaced. While there is no regulatory requirement for labeling secondary containers, prudent laboratory techniques make this a desirable practice. Use of formulas, codes, numbers, or symbols is encouraged for marking small containers.
- When the health effects of a chemical developed within a laboratory are unknown, that chemical shall be treated as a particularly hazardous substance.

- If a laboratory produces a chemical for a nonlaboratory user, then the "producer" is required to comply with the labeling and material safety data sheet (MSDS) provisions of the health hazard communication program (see Supplement 7.02).
- In research laboratories, MSDSs shall be accessible to chemical users but need not be physically present in the area. To obtain an MSDS, contact the Hazards Control MSDS Hotline at extension 3-2122 or your ES&H industrial hygienist. Send a copy of each MSDS that accompanies incoming shipments of hazardous materials to MSDS, L-384, for retention.
- Detailed chemical inventories are required by several regulations. For the most current requirements, contact the ES&H team leader.

3.2.4 Personal Protective Equipment

- Where necessary, procedures shall be prepared on the use of eye, skin, and body protection; respirators; and other protective gear. Eye protection must be worn by all persons, including visitors, in areas where hazardous chemicals are being handled. The appropriate clothing that shall be worn for a particular process depends on the activity being carried out and the circumstances under which it is being carried out. See the OSP for more specific details.
- Appropriate gloves shall be worn when there is a potential for contact with toxic materials. These gloves should be inspected for holes, blisters, and cracking before use and should be replaced periodically or when damaged or punctured.
- Employees shall be trained in the proper use of respirators and shall wear them whenever exposure by inhalation is likely to exceed OSHA or ACGIH limits.
- Chapter 10 of the *Health & Safety Manual* provides guidance on selecting and using personal protective equipment.

3.2.5 Emissions to the Environment

The responsible individual shall review operations for all potential emissions of hazardous materials to the environment. The ES&H team environmental analyst will help determine the environmental controls needed, if any, or the permits required.

3.2.6 Spills and Accidents

Respond promptly to all spills and accidents involving any hazardous chemical. Also, notify the area ES&H team whenever an accident or spill occurs, and call the Fire Department (dial 911 at Livermore and at Site 300) when any of the following occurs or when in doubt about the severity of the incident:

- An accident or spill involving hazardous material results in personnel injury.
- There is a release of hazardous material to the sewer system.

- Area personnel are unfamiliar with the hazards of the spilled material.
- The spilled material exceeds the amount two workers can handle in one hour, or if additional assistance or supplies are needed to contain and clean up the material.

Immediate responses

- *Eye contact.* Flush eyes promptly with water for 15 min or until the victim is taken for medical evaluation.
- *Skin contact.* Flush the affected area promptly with water and remove any contaminated clothing; seek medical attention if the symptoms persist.
- *Clean up.* Promptly clean up spills or leaks (or both) that are not emergencies and do not require the presence or assistance of the Fire Department (as previously described). Use the appropriate protective apparel, equipment, and disposal procedures.

For more specific details on incident responses, refer to the substance MSDS.

NOTE: A copy of the MSDS should accompany workers sent to the Health Services Department because of injury or potential exposure to a substance.

3.2.7 Storage

The primary storage concerns with all chemical materials are to minimize the amounts stored, to avoid contact between incompatible chemicals, and to ensure that hazardous storage conditions (e.g., light and heat) are not present. Specific storage procedures, however, will depend on the type of storage facility and the chemicals in use. Below are some standard storage practices.

- Do not store incompatible materials in the same cabinet. Acids, bases, flammables, oxidizers, and poisons are mutually exclusive categories. When a substance has multiple hazards, preference shall be given to the most acute or reactive property.
- Do not store food and chemicals in the same refrigerator. Label refrigerators used for chemical storage.
- Periodically check the container, label integrity, and the shelf-life expiration date of chemicals in storage. If deficient, these containers shall be correctly labeled before removing from storage areas.
- Do not store combustible packaging materials (e.g., cardboard) in a flammable-liquid storage cabinet.
- Do not overload storage cabinets.
- Store only the amount of materials needed for the near future (e.g., 3 months).
- Consider the technical requirements and implement seismic safety for chemical storage rooms, shelves, and cabinets.

For more information on storing hazardous chemicals, see Chapter 21 of the *Health & Safety Manual*.

3.2.8 Waste Disposal

- To protect the environment and the safety and health of all people, hazardous waste must be disposed of properly. Therefore, all laboratory workers who generate or handle hazardous, radioactive, or mixed waste must take EP0006, “Hazardous Waste Handling Practices.” The procedures learned in this course, including those described in the *Environmental Compliance Manual*, must be followed in laboratory workplaces.
- Employees must adhere to the disposal requirements below.
 - Do not pour hazardous or radioactive chemicals down a sanitary sewer. Retention system drains may be used only when specifically approved for such chemicals.
 - Place all wastes in the proper containers for disposal. Waste must be removed from laboratories regularly (see Chapter 9 of the *Environmental Compliance Manual*).
 - Before reassignment or termination, ensure that the chemicals and wastes you are responsible for are properly labeled, prepared for disposal, or assigned to someone who understands how to manage such materials. See Supplement 2.10 for more information.

4. Criteria for Determining and Implementing Control Measures to Reduce Employee Exposure to Hazardous Chemicals

The purpose of this section is to provide the framework for selecting control measures for minimizing the risk of chemical hazards. Given the enormous variety of hazardous materials and potential operations, it is not possible to specify here the safety practices needed for every possible situation. Chapter 2 of the *Health & Safety Manual* covers this subject in further detail and establishes the methods for performing hazards analyses. The guidelines that follow shall be adhered to when planning controls for operations.

4.1 Types of Controls

Chemical hazards are reduced through various control measures that work in unison to minimize exposure. These measures include the following (in order of preference):

- *Chemical substitution*—such as using a less hazardous compound.
- *Engineering controls*—such as containments, enclosures, ventilation systems, and facility design.

- *Administrative controls*—such as written safety procedures, training, limited access, and medical surveillance.
- *Personal protective equipment*—such as respirators, gloves, and chemical protective clothing.
- *Work practices*—such as personal hygiene and laboratory technique.

4.2 Selection of Controls

After preparing a hazards analysis, a combination of controls may be used based on the following factors:

- The inherent toxic and physical properties of the materials and their intended use.
- The possibility of unplanned outcomes, spills, and accidents.
- Workplace factors, such as existing ventilation and protective systems.
- Possible exposure routes (inhalation, skin or eye contact, or ingestion).
- Employee skills, training, and prior experience.

Consultation with program management and the ES&H team is usually necessary before selecting the final control measures. This is especially true for new operations and those that involve particularly hazardous substances (see the section entitled “Additional Protection for Particularly Hazardous Substances”).

5. Ensuring Performance of Fume Hoods and Other Protective Equipment

Specific measures shall be taken to ensure proper and adequate performance of fume hoods and other protective equipment, including alarm systems. The guidance in Chapter 12 of the *Health & Safety Manual* and its supplements shall be followed as a general rule. These documents include ventilation requirements and acceptance criteria for all new and modified facilities, as well as surveillance, maintenance, and system-failure procedures for existing facilities. Consult with the Plant Engineering Department and the ES&H team before making a change to existing systems or to obtain the criteria for unique experimental setups.

The area ES&H team conducts regular performance checks on all ventilation systems used for hazardous materials. Before each use, however, the user should verify that the system is operating properly and that an approval sticker is on the unit. Hoods that are not operating as intended shall not be used for hazardous procedures. Systems used for high-hazard materials (e.g., toxic, radioactive, and

flammable) shall have continuous monitoring devices to alert users to their less-than-adequate performance.

6. Employee Information and Training

The primary goals of the Laboratory's ES&H policy are to protect the health and safety of employees and the public and to prevent property damage. In addition, the OSHA laboratory standard stipulates that employees must be provided with specific information about the chemical hazards in their work area and trained on how to handle such chemicals. Thus, it is important for employees to receive the required training that will enable them to take every reasonable precaution in the performance of their work. This training must be conducted and documented in accordance with LLNL's *Training Program Manual* and the training plan for each directorate.

6.1 Required Information

The responsible individual shall provide employees with the following:

- Location of hazardous chemicals in the work area at the time of initial assignment and before each new assignment that involves chemicals to which the employee may be exposed.
- PELs or TLVs for any OSHA-regulated substance used in the employee's job assignment. For a list of the most current PELs and TLVs, contact the area ES&H team.
- Information on the effects, signs, and symptoms of exposure to any hazardous substance being used.
- Location and availability of standard reference materials on the hazards found in the individual laboratories, including safe handling, storage, and disposal procedures for those hazardous chemicals.
- Location of the OSHA laboratory standard. If necessary, contact the ES&H team for a copy of this standard.
- Location of the procedure that enables employees to see this Chemical Hygiene Plan.

To facilitate satisfying the above required information, a sample form is provided. It is recommended that the responsible individual complete the forms and give them to employees.

6.2 Required Training

The training required by this Chemical Hygiene Plan shall include the following:

- Methods and observations used to determine the presence or release of a hazardous chemical, such as monitoring conducted by the Hazards Control Department, continuous monitoring devices, and the visual appearance or odor of hazardous chemicals being used.
- Measures that employees can take to protect themselves from hazards. These include appropriate engineering and administrative controls, personal protective equipment, work practices, and emergency procedures.
- Physical and health hazards in the work area, including flammable and reactive materials, irritants and corrosives, acute poisons, chronic organic toxins, allergens, and genetic toxins.
- MSDSs and their contents.
- Proper labeling, storage, and waste-disposal practices.
- Applicable details of this Chemical Hygiene Plan (i.e., the individual elements and its availability).

This training can be accomplished through formal courses given by the Environmental Protection Department and the Hazards Control Department or informal on-the-job training, or both. All training must be documented in accordance with LLNL's *Training Program Manual*.

The training requirements for the OSHA laboratory standard are similar to those of the Laboratory's health hazard communication program (as described in Supplement 7.02 and course HS4050, "Health Hazards Communication for Supervisors").

The frequency for refresher training is not stipulated in the OSHA regulation. Therefore, departments and divisions are encouraged to evaluate the need for such training on a case-by-case basis and in accordance with other ES&H training in their directorate's training plan.

7. Preapproval of Operations

The FSP lists the categories of work authorized in each facility, those that require prior review, and those that require a supplemental OSP. The responsible individual shall review the FSP before beginning new operations to ensure that they are within the scope of the FSP. Operations that are not within the scope of the FSP shall be evaluated in accordance with Chapter 2 of the *Health & Safety Manual*.

8. Medical Consultation and Examination

Medical attention following an exposure to chemicals is provided through the Health Services Department. Consultation, examination, and treatment by licensed physicians and nurse practitioners are available to all employees. In the event of a known acute exposure, referral should be prompt to ensure that appropriate decontamination and medical care are provided on time.

Employees shall be referred to the Health Services Department if

- Signs or symptoms develop that may be related to handling a chemical (e.g., headaches, skin rashes, dizziness, nausea, or loss of coordination or motor control); a relationship shall be considered possible until appropriate evaluation indicates otherwise.
- Air monitoring indicates air levels that exceed the PEL or TLV.
- An event such as a spill, leak, or explosion results in a hazardous exposure.

Medical attention includes

- Medical history and examination.
- Specific treatment as necessary.
- Laboratory tests if required.
- Follow-up examination.

If an employee is referred to the Health Services Department for medical consultation or examination, management must provide the physician with

- The name and nature of any chemical that may be involved (including the MSDS).
- The conditions under which any possible overexposure occurred.
- Any monitoring or test results.
- A report of any signs or symptoms the employee or management has identified.

The Health Services Department examiner shall provide a written report to the employee's manager identifying

- Medical follow-up, if needed.
- The results of the medical examination and any associated tests.
- Any medical condition identified during the examination that may place the employee at increased risk as a result of exposure to hazardous chemicals found in the workplace.

- A statement that the employee has been informed by a physician of the results of the examination and of any medical condition that may require further examination or treatment.

NOTE: This report should not include specific findings of diagnoses unrelated to occupational exposure.

The Health Services Department shall only provide emergency and first-aid care to contract labor, contractors, consultants, and other non-LLNL employees. These individuals shall then be referred to their company's physician or private practitioner for further treatment, if necessary. Management must provide the contractor's physician with the chemical names and the condition of exposure, as previously described.

9. Designation of Chemical Hygiene Officer

The Hazards Control Department shall appoint a chemical hygiene officer for the Laboratory. See the section entitled "Responsibilities for Chemical Hygiene" in this supplement for more details.

The industrial hygienists for the ES&H teams shall

- Provide day-to-day guidance on issues related to chemical hygiene and safety.
- Coordinate activities related to the Chemical Hygiene Program with the Laboratory's chemical hygiene officer.

10. Additional Protection for Particularly Hazardous Substances

10.1 General

Special consideration shall be given to protecting employees from particularly hazardous chemicals. For the purposes of this supplement (LLNL Chemical Hygiene Plan for Laboratories), these include designated carcinogens, reproductive hazards, and acutely toxic materials (see Appendix A for definitions). The list of particularly hazardous chemicals is updated at least annually. For a current copy of this list, contact the ES&H team.

The precautions used to protect employees from exposure to particularly hazardous chemicals shall be specified within the FSP and OSP applicable to the area where such materials are used. Supplement 21.16A of the *Health & Safety*

Manual provides guidance for the safe handling of carcinogens and may be used as a recommended guide for handling other highly hazardous chemicals. Supplement 12.03 provides safety requirements for using hoods and glove boxes when toxic materials are handled.

10.2 Additional Protection Required

When particularly hazardous substances are used in laboratories, the controls below shall be implemented for additional protection. It is strongly recommended that the area ES&H team be contacted for assistance with identifying which substances are particularly hazardous and for guidance on selecting controls.

1. Establish “designated areas” (defined in Appendix A). The facility manager (or his/her designee) shall ensure that the appropriate warning signs are posted in these areas. The health hazard communication poster may be used to satisfy this requirement.
2. Use containment devices (e.g., fume hoods or glove boxes) when
 - Volatilizing listed substances.
 - Manipulating substances that may generate aerosols.
 - Using laboratory procedures that may result in an uncontrolled release of the substance.

High-efficiency particulate air (HEPA) filters, carbon beds, or scrubber systems shall be used with containment devices to protect effluent and vacuum lines, pumps, and the environment whenever feasible.

3. Establish procedures for the safe removal of contaminated waste. Disposal of any of the substances identified in this section is controlled by state or local regulations. If necessary, refer to Chapter 9 of the *Environmental Compliance Manual* for removal and disposal policies and guidelines, or contact the environmental analyst for your area ES&H team for guidance.
4. Develop decontamination procedures. To ensure that chemical residues do not remain on the body, clothing, or equipment, employees shall follow the protocols in the OSP upon completing work with particularly hazardous substances or in the event of accidental contact with such chemicals.
5. Inform employees of the hazards in designated areas. Ensure that employees who work in designated areas are authorized to do so, and that they are trained on how to handle the hazards in such areas. All training provided to employees shall be documented in accordance with LLNL’s *Training Program Manual*.

6. Ask the ES&H team to conduct air- and surface-contamination monitoring for new procedures or when working conditions have changed. The results will help determine if a regular surveillance program is necessary. Initial monitoring is required for the materials listed in Table 2 if there is reason to believe that exposure levels exceed OSHA-defined limits. Contact the your area ES&H team for monitoring assistance.

See sections C.2 through C.5 in Appendix C for additional recommended guidance for work involving hazardous chemicals.

Appendix A

Terms and Definitions

action level	A concentration designated in 29 CFR 1910, Subpart Z for a specific substance. This value is calculated as an 8-h, time-weighted average and initiates certain required activities (e.g., exposure monitoring and medical surveillance).
acute toxicity	The toxic effect of a substance that has a rapid onset, sharp or severe effects, and pronounced symptoms; this effect is not chronic.
American Conference of Governmental Industrial Hygienists (ACGIH)	An independent professional organization that prepares an annual list of recommended exposure guidelines for hazardous chemicals in the occupational setting. See "threshold limit value."
chemical hygiene plan	A written program developed and implemented by the employer that sets forth procedures, equipment, personal protective equipment, and work practices to (1) protect employees from the health hazards caused by hazardous chemicals used in a particular workplace, and (2) meet the requirements of paragraph (e) of 29 CFR 1910.1450.
chronic toxicity	The toxic effect of a substance that develops gradually, lasts for a long time, and may have a delayed onset after exposure; this effect is not acute.
combustible liquid	Any liquid having a flash point at or above 100° F (37.8° C) but below 200°F (93.3° C), except for mixtures having components with flash points of 200° F (93.3° C) or higher, the total volume of which makes up 99% or more of the total of the mixture.
compressed gas	(1) A gas or mixture of gases in a container that has an absolute pressure exceeding 40 psi at 70° F (21.1° C). (2) A gas or mixture of gases in a container that has an absolute pressure exceeding 104 psi at 130° F (54.4° C) regardless of the pressure at 70° F (21.1° C). 3) A liquid having a vapor pressure that exceeds 40 psi at 100° F (37.8° C), as determined by ASTM D-323-72.

designated area	An area that may be used for work with “select carcinogens,” reproductive toxins, or substances that have a high degree of acute toxicity. A designated area may be an entire laboratory, an area of a laboratory, or a device (e.g., a laboratory hood).
designated carcinogen	A carcinogen that meets the criteria for OSHA “select carcinogen” or falls into Category 1 or 2 of the ACGIH’s list of carcinogens.
emergency, chemical	An incident involving chemicals becomes an emergency whenever there is personnel injury; an unplanned release to the environment; an unplanned or uncontrolled fire, explosion; or significant property damage.
explosive	A chemical that causes a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature.
flammable chemical	<p>A chemical that falls into one of the following categories:</p> <p>(1) <i>Aerosol, flammable</i>—An aerosol that, when tested by the method described in 18 CFR 1500.45, yields a flammable projection that exceeds 18 in. at the full valve opening or a flashback (a flame extending back to the valve) at any degree of the valve opening.</p> <p>(2) <i>Gas, flammable</i>—(a) A gas that, at ambient temperature and pressure, forms a flammable mixture with air at a concentration of 13% or less by volume; or (b) a gas that, at ambient temperature and pressure, forms a range of flammable mixtures with air that is more than 12% of volume regardless of the lower limit.</p> <p>(3) <i>Liquid, flammable</i>—Any liquid having a flash point below 100° F (37.8° C), except for mixtures having components with flash points of 100° F (37.8° C) or higher, the total of which makes up 99% or more of the total volume of the mixture.</p> <p>(4) <i>Solid, flammable</i>—A solid, other than a blasting agent or explosive (as defined by 29 CFR 1910.109[a]), that may cause fire through friction, absorption change, or retained heat from manufacturing or processing, or that can be ignited readily and when ignited burns vigorously and persistently thereby</p>

creating a serious hazard. A chemical shall be considered to be a flammable solid if, when tested by the method described in 16 CFR 1500.44, it ignites and burns with a self-sustained flame at a rate greater than 0.1 in./sec along its major axis.

hazardous chemical

A chemical for which there is statistically significant evidence (based on at least one study conducted in accordance with established scientific principles) that acute or chronic health effects may occur if employees are exposed. The term "health hazard" includes chemicals that are carcinogens; toxic or highly toxic agents; reproductive toxins; irritants; corrosives; sensitizers; hepatotoxins; nephrotoxins; neurotoxins; agents that act on the hematopoietic systems; or agents that damage the lungs, skin, eyes, or mucous membranes.

high acute toxicity

Substances with the following effects (from 29 CFR 1910.1200):

- Median LD50 of 50 mg/kg orally in albino rats, total dosage 200-300 g.
- Median LD50 of 200 mg/kg by continuous contact for 24 h with the bare skin of albino rabbits weighing between 2 and 3 kg.
- Median LC50 in air of 200 ppm (or mg/l) continuous inhalation for 1 h.

laboratory

A facility where the "laboratory scale use of hazardous chemicals" occurs, or a workplace where relatively small quantities of hazardous chemicals are used on a nonproduction basis.

laboratory scale

Work with substances in which the containers used for reactions, transfers, and other handling of substances are designed to be easily and safely manipulated by one person. "Laboratory scale" excludes those workplaces whose function is to produce commercial quantities of materials.

laboratory use of hazardous chemicals

The handling or use of such chemicals where all of the following conditions are met:

- (1) Chemical manipulations are carried on a laboratory scale.
- (2) Multiple procedures or chemicals are used.

(3) The procedures involved are neither part of a production process nor in any way simulate one.

(4) "Protective laboratory practices and equipment" are available and are commonly used to minimize the potential for employee exposure to hazardous chemicals.

LC ₅₀	"Lethal concentration, 50%" is the statistical calculation of the airborne level of a substance that, if inhaled, is fatal to 50% of the test organisms. This concentration is usually expressed in units of mass over volume (mg/m ³) or in parts per million (ppm). Species and exposure conditions must be specified.
LD ₅₀	"Lethal dose, 50%" is the statistical calculation of the amount of a substance that is fatal to 50% of the test organisms. This value is usually expressed in units of mass per body weight of the tested species (e.g., mg/kg). Exposure route, species, and duration of exposure conditions must be specified.
organic peroxide	An organic compound that contains the bivalent -O-O- structure. Such a compound may be considered as a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms have been replaced by an organic radical.
oxidizer	A chemical, other than a blasting agent or explosive (as defined in 29 CFR 1910.109[a]), that initiates or promotes combustion in other materials, thereby causing fire of itself or through the release of oxygen or other gases.
particularly hazardous substances	For the purposes of this supplement, these include OSHA "select carcinogens," reproductive toxins, and substances with a high degree of acute toxicity.
permissible exposure level (PEL)	The OSHA exposure limits for hazardous chemicals in the workplace. These limits are contained in 29 CFR 1910, Subpart Z.
physical hazard	A chemical for which there is scientifically valid evidence that it is a combustible liquid, a compressed gas, an explosive, a flammable, an organic peroxide, an oxidizer, a pyrophoric, an unstable (reactive), or a water reactive.

protective laboratory practices and equipment	Laboratory procedures, practices, and equipment accepted by laboratory health and safety experts as effective, or those that employees can show to be effective in minimizing the potential for employee exposure to hazardous chemicals.
reproductive toxins	Chemicals that affect reproductive capabilities, including chromosomal damage (mutations) and effects on fetuses (teratogenesis). (For the purposes of the LLNL Chemical Hygiene Plan for Laboratories, these include any substance or exposure identified as reproductive toxins in the <i>Catalogue of Teratogenic Agents</i> ¹ and the State of California list of reproductive hazards under Proposition 65 [Ref. 2].)
select carcinogen	<p>Any substance that is</p> <ol style="list-style-type: none"> (1) regulated by OSHA as a carcinogen; (2) listed under the category “known to be carcinogens” in the National Toxicology Program’s (NTP’s) <i>Annual Report on Carcinogens</i>³; (3) listed under Group 1 (carcinogenic to humans) by the <i>International Agency for Research on Cancer (IARC) Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man</i>⁴; (4) listed in either Group 2A or 2B by IARC or under the category “reasonably anticipated to be carcinogens” by NTP. Such a substance causes statistically significant tumor incidence in experimental animals based on any of the following criteria: <ul style="list-style-type: none"> • After inhalation of 6-7 h per day, 5 days per week, for a significant part of a lifetime of levels less than 10 mg/m³. • After repeated skin application of less than 300 mg/kg of body weight per week. • After oral dosages of less than 50 mg/kg of body weight per day.
threshold limit value (TLV)	Airborne concentrations of substances to which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse health effects.

unstable (reactive)	A chemical that, in its pure state or as produced and transported, will vigorously polymerize, decompose, condense, or become self-reactive under conditions of shock, pressure, or temperature.
water reactive	A chemical that reacts with water to release a gas that is flammable or a health hazard.

References

1. Code of Federal Regulations, Title 29, Part 1910.1450, "Occupational Exposure to Hazardous Chemicals in Laboratories."
2. T. H. Shepard, *Catalogue of Teratogenic Agents*, 6 ed. (Johns Hopkins Press, Washington, DC, 1989).
3. State of California, "List of Reproductive Hazards," Proposition 65 (latest revision—updated every 6 months).
4. National Toxicology Program, *Annual Report on Carcinogens*, U. S. Department of Health and Human Services, U. S. Government Printing Office, Washington, DC (latest edition).
5. International Agency for Research on Cancer, "Group 1—Carcinogenic to Humans," in *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man*, World Health Organization Publications Center, Albany, NY (latest editions).

Appendix B

Sample Form for Providing Information to Employees

B.1 Locations of Documents

Supplement 21.01 of the *Health & Safety Manual* contains the LLNL Chemical Hygiene Plan for Laboratories. A copy of this plan is also kept in the following locations:

- Assurance managers' offices.
- Facility managers' offices.
- _____.

A copy of the OSHA laboratory standard can be obtained from your area ES&H team or the Hazards Control's Industrial Hygiene Group (ext. 2-1214).

B.2 Information on Hazardous Substances Used

Compound	PEL/TLV*	Effects of overexposure

* PEL = Permissible exposure level; TLV = Threshold limit value.

B.3 Standard Reference Material in this Work Area on Chemical Hazards

References	Location
1. Material safety data sheets	_____
2. <i>Merck Index</i> (by Merck and Company, Rahway, NJ)	_____
3. <i>Dangerous Properties of Industrial Materials</i> (by N. I. Sax, Van Nostrand Reinhold, NY)	a. Industrial Hygiene Group, ext. 2-1214, L-384 b. _____
4. List of particularly hazardous substances	a. Industrial Hygiene Group, ext. 2-1214, L-384 b. _____
5. _____	_____

Appendix C

Safe Practices and Procedures for Working with Chemicals

The guidance in this appendix is advisory. It supplements the requirements in the LLNL Chemical Hygiene Plan for Laboratories, may meet the specific needs of some laboratories, and may be useful for employee training and for preparing OSPs and FSPs. (Most of the information in this appendix were taken from Appendix A of 29 CFR 1910.1450, which summarizes material from the National Research Council's document, *Prudent Practices for Handling Hazardous Chemicals in Laboratories* [National Academy Press, Washington, DC, 1981].)

C.1 General Safe Practices

The general practices below shall be followed when working with chemicals in laboratories.

- Do not smell or taste chemicals.
- Vent apparatus (e.g., vacuum pumps and distillation columns) that may discharge toxic chemicals into local exhaust devices.
- Do not release toxic substances into cold or warm rooms; these rooms have contained, recirculated atmospheres.
- Handle and store laboratory glassware carefully to avoid damage; do not use damaged glassware. Use extra care with Dewar flasks and other evacuated glass apparatus; if necessary, shield or wrap them to contain chemicals and garments in case an implosion occurs. Use equipment only for its designed purpose.
- Carry hazardous chemicals in a secondary container.
- Wash areas of exposed skin well before leaving the laboratory.
- Avoid practical jokes or other behavior that might confuse, startle, or distract another worker.
- Confine long hair and loose clothing. Wear shoes at all times in the laboratory; sandals or perforated shoes are not permitted.
- Keep the work area clean and uncluttered; clean up upon completing an operation or at the end of each day. Properly label and store chemicals and equipment.
- Do not wear contact lenses in the laboratory. If it is necessary to do so, however, inform your supervisor so that he/she can take special precautions.
- Remove laboratory coats immediately after contamination.

- Keep materials stored in hoods to a minimum; do not allow materials to block vents or the air flow.
- Leave the hood “on” when not in use, especially if it contains toxic substances or if you are uncertain whether adequate general laboratory ventilation will be maintained when the hood is “off.”

C.2 Work with Chemicals of Moderate, Chronic, or High-Acute Toxicity

The precautions below shall be taken when working with chemicals of moderate, chronic, or high-acute toxicity. Examples of these substances include diisopropylfluorophosphate, hydrofluoric acid, and hydrogen cyanide.

- Use all reasonable precautions to minimize exposure to these toxic substances.
- Always use a hood (that has been previously evaluated to confirm adequate performance) or other containment devices for procedures that may generate aerosols or vapors containing the substance; if possible, trap released vapors to prevent discharge.
- Always avoid skin contact with these materials; use gloves, long sleeves, and other protective apparel as appropriate. Always wash hands and arms immediately after working with these materials.
- Ensure that at least two people are present at all times if a compound in use is highly toxic or its toxicity is unknown.
- Store breakable containers with these substances in chemically resistant trays; also, operate and mount apparatus above such trays or cover work and storage surface with removable, absorbent, plastic-backed paper.

C.3 Work with Chemicals of High Chronic Toxicity

The precautions below shall be taken when working with chemicals of high-chronic toxicity. Examples of such substances include dimethylmercury and nickel carbonyl, benzo[a]pyrene, N-nitrosodiethylamine, and other human carcinogens or substances with high carcinogenic potency in animals.

- Conduct all transfers and work with these substances in a “controlled area” (e.g., a restricted access hood, glove box, or part of a laboratory designated for working with such substances). Ensure that all persons with access to controlled areas are aware of the substances being used and the precautions required.
- Protect vacuum pumps from being contaminated by scrubbers of HEPA filters; vent them into the hood.
- Decontaminate the controlled area before normal work is resumed.

- Remove any protective apparel and thoroughly wash hands, forearms, face, and neck before leaving a controlled area. Place the apparel in an appropriately labeled container.
- Use a wet mop or a vacuum cleaner with a HEPA filter if the toxic substance is a dry powder; do not dry sweep.
- Consult with the Health Services Department about regular medical surveillance if you often use large quantities of toxic substances.
- Ensure that the controlled area is conspicuously marked with warning and restricted access signs, and that all containers with these substances are appropriately identified and have warning labels.
- Ensure that contingency plans, equipment, and materials are available to minimize exposures to people and property if an accident occurs.
- Store chemicals in unbreakable, chemically resistant, secondary containers. Label the containers appropriately and store them in a ventilated, limited-access area.

C.4 Work with Allergens and Embryotoxins

The precautions below shall be taken when working with allergens and embryotoxins.

- Review each use of these materials with the research supervisor; review continuing uses annually or whenever a procedural change is made.
- Properly label these substances; store them in an unbreakable secondary container in an adequately ventilated area.
- Notify supervisors of all incidents of exposure or spills; consult a qualified physician when appropriate.

Examples of and the requirements for these substances are as follows:

Allergens (e.g., diazomethane, isocyanates, and bichromates)—Wear suitable gloves to prevent hand contact with allergens or substances of unknown allergenic activity.

Embryotoxins (e.g., organomercurials, lead compounds, and formamide)—If you are a woman of childbearing age, only handle these substances in a hood that functions properly. Use appropriate protective apparel (especially gloves) to prevent skin contact.

C.5 Animal Work with Chemicals of High-Chronic Toxicity

The following precautions shall be taken when animal work involves chemicals of high-chronic toxicity:

- Administer the substance by injection or gavage instead of in the diet, when possible. If the substance is administered by diet, use a caging system under negative pressure or under laminar air flow directed toward HEPA filters.
- Develop procedures that minimize the formation and dispersal of contaminated aerosols, including those from food, urine, and feces. Use HEPA-filtered vacuum equipment for cleaning; moisten contaminated bedding before removal from the cage; mix diets in closed containers in a hood.
- Wear plastic or rubber gloves and fully buttoned laboratory coats or jumpsuits when working in the animal room. Other apparel and equipment (e.g., shoe and head coverings or respirators) may be used because of incomplete suppression of aerosols.

NOTE: Special facilities with restricted access are preferred for large-scale studies.